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PROCESS FOR TREATING CELLULOSIC TEXTILE MATERIAL

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This invention relates to a novel process for treating textiles. More particularly, this invention is concerned with a novel method for applying crosslinking agents to cellulosic textiles for the production of wash and wear fabrics.

It has been common practice to treat a cotton or other cellulosic fabric by various methods to render the fabric wrinkle resistant and to impart to the fabric good crease-retention and wash and wear characteristics. The materials which have been employed to effect these treatments include urea-formaldehyde resins, melamine-formaldehyde resins, dimethylol ethylene urea resins, acetals such as a modified glycol acetal, epoxides such as vinylcyclohexene dioxide, triazones such as tetrahydro-s-triaza-2(1H)-ones, triazines such as methoxymethylated melamine, divinyl sulfone and derivatives thereof, and the like. These treatments are generally effected by impregnating the fabric with an aqueous solution or suspension of the treating agent, a catalyst and auxiliary chemicals, such as softeners, by various techniques such as padding, spraying, immersion and the like. The impregnated fabric is then stretched to the desired width on a frame, dried and then cured by heating at elevated temperatures.

The mechanism by which the various treatments impart wash and wear characteristics to the treated fabric is not entirely clear, and may involve both crosslinking of cellulose molecules or resin deposition on the fibers. However, it is generally agreed that, to be effective, the treating agent must penetrate the fiber and crosslink the cellulose chains to some extent, thereby inhibiting intermolecular slippage of the cellulose molecules.

Regardless of the mechanism of the treatment, however, the conventional methods for effecting impregnation of the fabric with the treating agent have not been completely satisfactory. For example, recently there have appeared the so-called "permanently creased" garments such as trousers, pleated skirts and the like, in which curing is effected after the garment has been made, generally by pressing the garment to the desired configuration at temperatures sufficient to effect curing. These garments can be made by employing "presensitized" fabrics prepared by the textile finisher; i.e., fabrics which have been impregnated with a treating agent and then dried but not cured, which are susceptible to subsequent curing in any desired shape. In general, however, these presensitized fabrics are not completely stable, and may be susceptible to slow curing prior to fabrication of the garment, loss of treating agent, or both. On the other hand, if the conventional "wet method" of impregnation is effected by the garment manufacturer, the impregnated garment must be dried to remove excess water before curing. The pressing of the wet garment involves practical difficulties in pressing, and reduces the rate of production. In addition, pressing of the wet garment may result in difficulties caused by migration; the treating agent migrates to the surface of the fibers during evaporation of the solvent (usually water) and is cured there, resulting in a non-uniform treatment and often a harsher hand than is desired.

It has been discovered by this invention that these difficulties are avoided if the treatment is effected by spray-

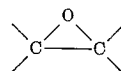
ing the treating agent in the absence of diluent on a "non-aqueous fabric." By the term "non-aqueous fabric," as employed herein, is meant a fabric having little or no liquid water on its surface. For example, it is known that the equilibrium moisture regain (moisture content based on bone dry fabric) at 100% relative humidity is approximately 24% for unmercerized cotton, and about 38% for mercerized cotton. Thus, mercerized cotton with a moisture regain of about 40% contains little or no liquid water on its surface. This regain moisture present in the fibers is sufficient to permit the treating agent to penetrate the fiber and allows curing to be effected directly after treatment without the intermediate drying step required when there is water on the surface. As a result, there is less danger of the deposition of treating agent at or on the surface of the fibers and the resulting harsh hand.

The method of this invention can be employed for all treatments of textiles in which penetration of the fiber is desired, such as impregnation with reagents to improve anti-static properties, dyes, mildewcides, flameproofing agents and the like. It is preferably employed for the treatment of cellulosic textile materials with polyepoxides to impart wash and wear properties and wrinkle resistance to the fabric.

By the term "cellulosic textile materials," as employed herein, is meant fibers, films, filaments, formed fabrics, woven and non-woven, felted, or otherwise classified textile materials containing at least 50% cellulose, including cotton, regenerated cellulose, jute, hemp, sisal, linen and the like and mixtures thereof.

The treatment with epoxides of this invention comprises generally spraying an undiluted liquid polyepoxide on a cellulosic fabric containing a cure-promoting amount of a catalyst under conditions such that the water content of the fabric does not exceed an amount sufficient to form liquid water on the surface of the fabric; e.g. not greater than 40 weight percent of the dry fabric in the case of mercerized cotton. The fabric should contain at least 5 weight percent water to swell the cellulose fibers and permit penetration of the polyepoxide. The optimum water content is the equilibrium regain at 100% relative humidity and room temperature; about 30 weight percent for mercerized cotton.

The polyepoxides employed in the process of this invention are normally-liquid materials possessing more than 1 vic-epoxy group, i.e. more than one



group. They may be aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted if desired with non-interfering substituents, such as chlorine atoms, hydroxyl groups, ether radicals and the like. They may also be monomeric or polymeric, provided they have a molecular weight of not greater than about 300. Polyepoxides having a molecular weight in excess of about 300 are generally too large to penetrate the fibers. By the term "normally liquid," as employed herein, is meant a compound which is liquid at room temperature and pressure.

The polyepoxides may be exemplified by the following: vinyl cyclohexene dioxide, epoxidized mono-, di and triglycerides, butadiene dioxide, 1,4-bis(2,3-epoxypropoxy)benzene, 1,3-bis(2,3-epoxypropoxy)benzene, 4,4'-bis(2,3-epoxypropoxy)diphenyl ether, 1,8-bis(2,3-epoxypropoxy)octane, 1,4-bis(2,3-epoxypropoxy)cyclohexane, 4,4'-bis(2-hydroxy-3,4-epoxybutoxy)diphenyldimethylmethane, 1,3-bis(4,5-epoxypentoxy)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chloro-

cyclohexane, diglycidyl thioether, diglycidyl ether, ethylene glycol diglycidyl ether, resorcinol diglycidyl ether, 1,2,5,6 - diepoxyhexene - 3, 1,2,5,6 - diepoxyhexane, and 1,2,3,4 - tetra(2 - hydroxy - 3,4 - epoxybutoxy) butane.

Other examples include the glycidyl polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess, e.g., 4 to 8 mol excess, of a chlorohydrin, such as epichlorohydrin and diglycerol chlorohydrin. Thus, the diglycidyl ether of 2,2-bis(2,3-epoxypropoxyphenyl)propane is obtained by reacting bis-phenol 2,2-bis(4-hydroxyphenyl)propane with an excess of epichlorohydrin in an alkaline medium. Other polyhydric phenols that can be used for this purpose include resorcinol, catechol, hydroquinone, methyl resorcinol, or polynuclear phenols, such as 2,2-bis(4-hydroxyphenyl)butane, 4,4'-dihydroxybenzophenone, bis(4 - hydroxyphenyl)ethane, and 1,5-dihydroxynaphthalene.

Still a further group of the polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in the presence of an acid-acting compound such as hydrofluoric acid, one of the aforescribed halogen-containing epoxides with a polyhydric alcohol, and subsequently treating the resulting product with an alkaline component. Polyhydric alcohols that may be used for this purpose include glycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol, sorbitol, mannitol, pentanetriol, pentaerythritol, di- and tripentaerythritol, polyglycerol, dulcitol, inositol, carbohydrates, methyltrimethylolpropane, 2,6-octanediol, 1,2,4,5-tetrahydroxycyclohexane, 2-ethyl-1,2,6-hexanetriol, glycerol methyl ether, glycerol allyl ether, polyvinyl alcohol and polyallyl alcohol, and mixtures thereof. Such polyepoxides may be exemplified by glycerol triglycidyl ether, mannitol tetraglycidyl ether, pentaerythritol tetraglycidyl ether and sorbitol tetraglycidyl ether.

Other polyepoxides include the polyepoxypolyhydroxy polyethers obtained by reacting, preferably in an alkaline medium, a polyhydric alcohol or polyhydric phenol with a polyepoxide, such as the reaction product of glycerol and bis(2,3-epoxypropyl)ether, the reaction product of sorbitol and bis(2,3-epoxy-2-methylpropyl)ether, the reaction product of pentaerythritol and 1,2 - epoxy - 4,5-epoxypentane, and the reaction product of bis-phenol and bis(2,3 - epoxy - 2 - methylpropyl)ether, the reaction product of resorcinol and bis(2,3-epoxypropyl)ether, and the reaction product of catechol and bis(2,3-epoxypropyl) ether.

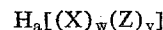
A group of polymeric-type polyepoxides comprises the hydroxy-substituted polyepoxy polyethers obtained by reacting, preferably in an alkaline medium, a slight excess, e.g., 0.5 to 3 mol excess, of a halogen-containing epoxide as described above, with any of the aforescribed polyhydric phenols, such as resorcinol, catechol, bis-phenol, bis[4 - (2'-hydroxynaphth - 1 - yl) - 2,2 - hydroxynaphth-1-yl]methane and the like.

The amount of polyepoxide employed is not highly critical, and effective amounts can vary from about 1 up to about 15 or more weight percent dry add-on after curing, based on the weight of the fabric. Amounts of less than about 1 percent generally fail to improve fabric properties, and amounts of greater than about 15 percent generally result in a harsh and boardy hand.

Curing agents that may be employed include acid-acting curing agents, such as inorganic acids and their salts; including phosphoric acid, boric acid, sulfonic and phosphonic acids, perchloric acid, persulfuric acid, boron-trifluoride complexes, such as the p-cresol and urea complex, zinc fluoborate, magnesium fluoborate, magnesium perchlorate, potassium persulfate, copper fluoborate, copper persulfate, cobaltic fluoborate, chromic nitrate, magnesium nitrate, calcium phosphite, and the like.

Preferred curing agents to be employed are the salts of metals of groups I to IV and VIII of the Periodic Table of Elements and inorganic acids the anion portion of which contains at least two dissimilar elements having an

atomic weight above 2, and particularly inorganic acids of the formula



wherein X is a non-metal having an atomic weight above 2, Z is an element which tends to gain from 1 to 2 electrons in its outer orbit, such as oxygen and fluorine; w is an integer; y is an integer greater than 1 and a equals the valency of the radical $(X)_w(Z)_y$, such as sulfuric acid, fluoboric acid, fluosilicic acid, persulfuric acid, phosphoric acid and the like.

The amount of the curing agent employed will vary depending upon the type of agent selected. In general, the amount of the curing agent will vary from about 0.5% to 30% by weight of the polyepoxide. The acids are preferably employed in amounts varying from about 0.5% to 20%, the metal salts are preferably employed in amounts varying from about 1% to 15%.

Examples of suitable salts include, among others, zinc fluoborate, copper fluoborate, magnesium fluoborate, aluminum fluoborate, nickel fluoborate, cadmium fluoborate, cerium fluoborate, strontium fluoborate, iron fluoborate, cobalt fluoborate, chromium fluoborate, mercury fluoborate, lead fluoborate, tin fluoborate and beryllium fluoborate, zinc sulfate, magnesium sulfate, copper sulfate, aluminum sulfate, nickel sulfate, cadmium sulfate, cerium sulfate, strontium sulfate, calcium sulfate, iron sulfate, cobalt sulfate, chromium sulfate, mercury sulfate, beryllium sulfate, tin sulfate and selenium sulfate, zinc sulfite, magnesium sulfite, copper sulfite, nickel sulfite, cerium sulfite, calcium sulfite, iron sulfite, cobalt sulfite, beryllium sulfite, tin sulfite, and selenium sulfite, copper persulfate, zinc persulfate, strontium persulfate, tin persulfate and cobalt persulfate, zinc nitrate, magnesium nitrate, copper nitrate, aluminum nitrate, cadmium nitrate, strontium nitrate, calcium nitrate, iron nitrate, cobalt nitrate, mercury nitrate, beryllium nitrate, lead nitrate, and tin nitrate, zinc fluoberyllate, magnesium fluoberyllate, iron fluoberyllate, strontium fluoberyllate, chromium fluoberyllate, zinc fluosilicate, copper fluosilicate, aluminum fluosilicate, chromium fluosilicate, cerium fluosilicate, selenium fluosilicate, zinc borate and aluminum borate, zinc phosphate, magnesium phosphate, nickel phosphate, cadmium phosphate, cerium phosphate, strontium phosphate, cobalt phosphate and mercury phosphate, zinc phosphite, mercury phosphite, copper phosphite, iron phosphite, zinc perchlorate, iron perchlorate, cobalt perchlorate, nickel perchlorate, zinc chlorate, iron chlorate, aluminum chlorate and tin chlorate. The salts may be in their anhydrous or hydrated form. Particularly preferred as catalysts are the water soluble salts.

Especially preferred are the above-noted salts of sulfuric acid, fluoboric acid, perchloric acid and phosphoric acids.

The polyepoxide can be sprayed on the fabric by any convenient technique. A suitable method comprises the use of an aerosol bomb containing the polyepoxide and a suitable propellant under sufficient pressure to force the epoxide out of the container in the form of a fine spray.

Any organic material which is inert toward the polyepoxide and which has a vapor pressure of from about 5 p.s.i.g. to about 300 p.s.i.g., preferably from about 30 to about 80 p.s.i.g., at 70° F. can be employed as the propellant. Suitable compounds include propane, n-butane, iso-butane, cyclobutane, vinyl chloride, dimethyl ether, dichlorotetrafluoroethane, dichlorodifluoromethane, chlorodifluoromethane, or mixtures of compounds having the aforementioned vapor pressures, such as 50/50 fluorotrichloromethane/difluorodichloromethane, 15/75/10 dimethyl ether/dichlorodifluoromethane/fluorotrichloromethane, 45/45/10 fluorotrichloromethane/dichlorodifluoromethane/isobutane and the like. The preferred propellant system consists of from 40 to 60 weight percent monofluorotrichloromethane and from 60 to 40 weight percent difluorodichloromethane, with a 50/50 mixture being particularly preferred.

In general the aerosol composition contains at least 40 weight percent propellant, with the balance consisting of polyepoxide and any other desired additives such as softeners, fluorescent brighteners and the like. Propellant amounts of from 40 to 60 weight percent are preferred.

As an alternative, the polyepoxide can be sprayed on the fabric using air pressure and an appropriate spray nozzle, thus obviating the need for a chemical propellant.

The method of this invention can find utility in a number of ways. For example, the fabric finisher can impregnate the fabric with the curing catalyst by employing an aqueous solution containing the catalyst for the final rinsing of the fabric. The resulting sensitized fabric can then be formed into a garment, sprayed with epoxide and cured by the garment manufacturer. Other applications will readily occur to those skilled in the art.

aerosol formulation similar to that employed in Example 1, except that vinylcyclohexene dioxide was substituted for the bis(epoxybutyl)ether, to about 11 percent nominal add-on. One sample of each of the treated materials having 7 and 30 percent regain was heated at 150° C. for 3 minutes (Cure Method A). The remaining samples were wrapped in polyethylene film, allowed to stand at room temperature for one hour and heated at 150° C. for 3 minutes (Cure Method B). After washing, drying and conditioning the samples were evaluated for wash and wear characteristics. The data from these experiments are set forth below, together with data obtained from a sample treated by padding to 97 weight percent pick up with a solution of 12 weight percent vinylcyclohexene dioxide, 1 weight percent zinc fluoborate and 0.3 weight percent zinc oxide, drying at 75° C. for 3 minutes and curing by heating at 150° C. for 3 minutes. (Method C).

Cure Method	Regain, Percent	Dry Add-On, Percent	Dry Crease Recovery, Percent	Wash-Wear Index		Breaking Strength, Percent	Bending Length, cm.
				Tumble Dry	Spin Dry		
A-----	7	2.0	40	1	2-	34	1.5
A-----	30	10.2	70	4	2	60	1.4
B-----	7	7.4	60	4-	2-	51	1.4
B-----	30	9.2	68	4	3-	58	1.5
C-----		7.4	64	4	2	53	1.4

The following examples are illustrative:

Example 1

A piece of mercurized cotton printcloth was padded to 104 weight percent wet pick-up with a 1.0 weight percent aqueous solution of zinc fluoborate and then air-dried until there was present only 16 weight percent water, based on bone dry fabric (16 percent regain). One side of the fabric was then sprayed with an aerosol composition consisting of 50 weight percent bis(3,4-epoxybutyl)ether, 25 weight percent monofluorotrichloromethane and 25 weight percent difluorodichloromethane under 40 p.s.i.g. pressure to a nominal add-on of 17 weight percent of the diepoxide. The sprayed fabric was then cured by heating at 120° C. for 3 minutes, washed, dried and then evaluated. The fabric had an 11.7 percent dry add-on, a dry warp crease recovery of 81 percent, tumble-dry and spin-dry washwear indices of 5 and 4+, respectively, retained 52 percent of its original filling breaking strength and had a bending length of 1.5 cm.

The experiment was repeated, except that the fabric, before spraying, contained 27 weight percent water, based on bone-dry fabric. The results of the test evaluation on this fabric are summarized in tabular form below, together with the test results of the above-described experiment and an untreated sample.

Percent Water Before Spraying	Dry Add-On, Percent	Dry Crease Recovery, Percent	Wash-Wear Index		Breaking Strength, Percent	Bending Length, cm.
			Tumble Dry	Spin Dry		
16	11.7	81	5	4+	52	1.5
27	12.6	82	5-	4+	57	1.5
-----	-----	34	1-	1-	100	1.6

Example 2

Employing procedures similar to those described in Example 1, four samples of mercerized cotton printcloth were padded to 101 weight percent wet pick-up with an aqueous solution containing 1.0 weight percent zinc fluoborate and 0.3 weight percent zinc oxide. Two samples were air dried to 30 percent regain and the other two to 7 percent regain. Each sample was sprayed with an

From this example it can be seen that the fabric treated in accordance with this invention has wash and wear properties which are at least as good as those obtained by the prior art method, even when the fabric contains as little as 7 weight percent water, provided sufficient time is provided to permit diffusion of the epoxide treating agent throughout the fabric fibers.

Example 3

Three samples of mercerized cotton printcloth were padded to about 98 percent wet pick-up with a solution of 1.5 weight percent zinc fluoborate and 1.0 weight percent magnesium oxide, and then air dried to about 30% regain. Each sample was then sprayed to 11 percent nominal add-on with an aerosol composition similar to that described in Example 1, except that 1,2,7,8-diepoxyoctane, which has a solubility in water of only 6 percent, was substituted for the bis(epoxybutyl)ether. After curing at 120° C. for 3 minutes, laundering and drying, the fabrics had an average dry add-on of 8.2 percent, a crease retention of 77 percent, wash and wear tumble dry and spin dry indices of 5 and 4, respectively, and a filling breaking strength retention of 48 percent.

Example 4

Mercerized cotton printcloth was padded to approximately 100 weight percent wet pick-up with an aqueous

solution containing 2.0 weight percent zinc fluoborate and 0.3 weight percent zinc oxide, and air dried to 30 percent regain. The fabric was then sprayed to a nominal add-on of 5.7 weight percent with an aerosol composition similar to that described in Example 1, except that bis(2,3-epoxycyclopentyl)ether, which has a water solubility of only 0.3 percent, was substituted for the bis(epoxybutyl)ether. The sprayed fabric was wrapped in polyethylene film, held at room temperature for 30 min-

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utes and cured by heating at 140° C. for 3 minutes. The cured fabric, after laundering and drying, had a dry add-on of 4.5 weight percent, a dry warp crease recovery of 59 percent, wash-wear tumble dry and spin dry indices of 3+ and 2, respectively, a retained filling breaking strength of 47 percent and a soft hand.

The tests employed in the examples were:

A. *Dry crease recovery*.—ASTM D1295-60T (warp direction only).

B. *Wash-wear index*.—AATCC tentative test method 88A-1962T.

C. *Breaking strength*.—ASTM D39-49 (warp direction only by raveled strip method).

D. *Bending length*.—ASTM D1388-55T (cantilever test).

What is claimed is:

1. In the method for imparting wash and wear properties to a cellulosic fabric which comprises impregnating said fabric with a polyepoxide and a curing catalyst and thereafter curing the impregnated fabric, the improvement of effecting the impregnation of said fabric with said polyepoxide by spraying liquid non-aqueous polyepoxide on the surface of a cellulosic fabric which contains at least about 5 percent by weight of regain water, based on the bone dry weight of the fabric, and which is free of water other than water of regain in the fibers thereof.

2. The method as described in claim 1 wherein said cellulosic fabric contains an amount of water substantially equivalent to the equilibrium regain at 100 percent relative humidity and room temperature.

3. The method as described in claim 1 wherein said polyepoxide is vinyl cyclohexene dioxide.

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4. The method as described in claim 1 wherein said polyepoxide is applied to said fabric as an aerosol composition comprising a normally-liquid polyepoxide in admixture with a propellant having a vapor pressure of from 5 to 300 p.s.i.g. at 70° F.

5. In the method for imparting wash and wear properties to a cotton fabric which comprises impregnating said fabric with a polyepoxide and a curing catalyst and thereafter curing the impregnated fabric, the improvement of effecting the impregnation of said fabric with said polyepoxide by spraying liquid non-aqueous polyepoxide on the surface of a cotton fabric which contains at least about 5 percent by weight of regain water, based on the bone dry weight of the fabric, and which is free of water other than water of regain in the fibers thereof.

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